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The Effect of Stress on the Microwave Dielectric Properties of $Ba_{0.5}Sr_{0.5}TiO_3$ Thin Films

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Abstract. Single phase, (1 0 0) epitaxial $Ba_{0.5}Sr_{0.5}TiO_3$ (BST) films have been deposited onto (1 0 0) $LaAlO_3$ and MgO substrates by pulsed laser deposition (PLD). The capacitance and dielectric losses of as-deposited and annealed films have been measured from 1–20 GHz as a function of electric field (0–80 kV/cm) at room temperature. The dielectric properties are strongly affected by the substrate type, post-deposition annealing time (≤ 6 h) and temperature (≤ 1200°C). For epitaxial BST films deposited onto MgO, it is observed that, after a post-deposition anneal the dielectric constant and the dielectric loss decreases. For epitaxial BST films deposited onto LAO, a post-deposition anneal (≤ 1000°C) results in an increase in the dielectric constant and an increase in the dielectric loss. The dc electric field induced change in the dielectric constant tends to increase with the dielectric constant and is largest for as-deposited films on MgO and post-deposited annealed films on LAO. In general, for epitaxial BST films, a large electric field effect is observed in films that have a large dielectric loss and a small electric field effect in films that have a low dielectric loss. High resolution X-ray diffraction measurements indicate that deposited film exhibit a significant tetragonal distortion which is strongly affected by a by a post deposition anneal. The observed differences in dielectric properties of the epitaxial BST films on MgO and LAO are attributed to the differences in film stress which arise as a consequence of the lattice mismatch between the film and the substrate and the differences in the thermal coefficient of expansion between the film and the substrate. A thin amorphous buffer layer of BST has been used to relieve stress induced by the lattice mismatch between the film and the substrate. Unlike epitaxial films, stress relieved films do not show an inverse relationship between dielectric tuning and Q ($1/\tan\delta$) and may be superior materials for tunable microwave devices.

Keywords: ferroelectric thin films, $(Ba,Sr)TiO_3$, pulsed laser deposition, microwave dielectrics, loss tangent, strain

Introduction

Ferroelectric (FE) thin films offer a unique opportunity for the development of tunable microwave signal processing devices. In a ferroelectric, the dielectric constant can be reduced by more than a factor of 2 in the presence of a dc electric field (< 200 kV/cm) [1–4]. The field dependent change of the dielectric constant can be used to produce a shift in a resonant frequency, time delay or a phase shift in an electronic device. Most tunable RF circuits currently rely on a variable capacitance device such as a GaAs varactor. Semiconducting varactors suffer from a number of disadvantages, the most serious being that the devices are inherently lossy at microwave frequencies and the loss increases with frequency. It is expected that a voltage controlled dielectric based device will offer a low power, low loss alternative to semiconducting based devices because the loss should only be determined by the frequency independent dielectric loss.

The solid solution ferroelectric, $Ba_xSr_{1-x}TiO_3$ (BST), is well suited for the development of FE based microwave electronics [5,6]. A large electric field effect has been observed in BST thin films for fields ≤ 200 kV/cm [7,8]. At issue in the development of microwave devices based on ferroelectric thin films is the magnitude of the change in the dielectric constant with the applied field and the dielectric loss. Epitaxial thin films of BST have been deposited onto dielectric substrates using pulsed laser deposition (PLD) [9]. The structure and morphology have been measured using X-ray diffraction (XRD) and scanning electron microscopy (SEM). The dielectric properties of BST $(x = 0.5)$ thin films have been measured at microwave frequencies (1–20 GHz), as a function of substrate type MgO and $LaAlO_3$ (LAO) and electric field ($\leq$ 80 KV/cm). The dielectric properties were measured for both as-deposited films and films which had been annealed in flowing oxygen ($T \leq 1200$°C). A correlation is observed between the dielectric constant, the electric field effect (% change in the dielectric constant) and the stress in the deposited film. In epitaxial films, an inverse relationship is observed between the dielectric constant and the dielectric Q (1/tanδ). However, in films in which the stress has been relieved, the inverse relationship is not observed. Strain relieved films are more suitable for the development of tunable microwave devices.

Experimental

$Ba_{0.5}Sr_{0.5}TiO_3$ thin films (~ 5000 Å) were grown on single crystal (1 0 0) MgO and (LAO) single crystal substrates at 750°C in an oxygen ambient pressure of 350 mTorr by pulsed laser deposition (PLD) [10]. The BST films were post-deposition annealed in flowing O_2 at 900–1000°C for 24 h. Films were also annealed at 1050–1250°C for 2 h using an encapsulated-sample annealing technique [11]. The latter annealing technique was developed, especially for a higher temperature ($\geq$ 1100°C) annealing, to prevent film surface degradation and stoichiometric loss. BST films were characterized for structure and morphology using XRD and SEM. Film composition was determined by inductively coupled plasma-optical emission spectroscopy (ICP). Interdigitated capacitors with gaps from 6 to 12 μm were deposited on top of the BST films through a polymethylmethaacrylate (PMMA) lift off mask by e-beam evaporation of 1–2 μm thick Ag and a protective thin layer of Au. Microwave S_{11} measurements were made on a HP 8510C network analyzer at room temperature. The data are fitted to a parallel resistor-capacitor model to determine capacitance and dielectric Q. Dielectric constants (ε) were calculated from the device dimensions [12].

Results and Discussion

BST $(x = 0.5)$ films grown on (1 0 0) MgO and LAO substrates at 750°C in 350 mTorr of oxygen were found by XRD to be single phase and exclusively epitaxial in the (1 0 0) direction [9]. Typical full width half maximum (FWHM) of the ω-scan peaks for the (0 0 2) reflection of BST films on (1 0 0) MgO were 0.7° to 0.9°. For films deposited onto LAO, ω(FWHM) was 0.16° (the resolution limit of the diffractometer). X-ray diffraction also indicates that the films are epitaxial in the plane of the substrate. From the XRD data, it was determined that the as-deposited films had larger lattice parameters than the bulk BST, presumably due to oxygen deficiency. Post deposition annealing of deposited films in O_2 caused the lattice parameter to decrease approaching the bulk value as oxygen vacancies were filled. As the annealing temperature increased, ω-scan FWHMs for BST films on MgO reached a minimum of ~ 0.4°. In addition to oxygen vacancies, the BST $(x = 0.5)$ films were Ba and Sr deficient, (Ba/Ti = 0.45 and Sr/Ti = 0.49), as determined by ICP. SEM images of as-deposited BST films on MgO and LAO showed that both films were fine grained with an average grain size of ~ 500 Å. Films deposited from compensated targets (targets which had an excess of Ba and Sr) did not show a significant increase in the film content of Ba and Sr. However, these films did show a significant increase in the grain BST grain size (1000–2000 Å).

The dielectric properties of BST films deposited onto MgO and LAO are significantly different, as shown in Table 1. At zero field, for the same capacitor geometry, the as-deposited BST film on MgO shows a higher capacitance and a lower dielectric Q than the as-deposited BST film on LAO ($\varepsilon = 1540 \pm 382$ and 874 ± 54 respectively). The reported values for capacitance and Q are nominally at 10 GHz although most of the samples were very stable over the whole frequency range (1–20 GHz). The dielectric Q is low for the as-deposited film on MgO compared to a similar film deposited onto LAO. Annealing the films in flowing oxygen caused a significant change in the dielectric properties. On MgO the capacitance is reduced and the dielectric Q is increased. The opposite behavior is observed for BST films on LAO.

Table 1. Dielectric properties measured at 1–20 GHz as a function of electric field (0–67 kV/cm) of as-deposited and low-temperature ($\leq 1000°C$) annealed BST ($x = 0.5$) films on MgO and on LAO. The number of device measurements is 12 and 21 for BST on MgO and LAO, respectively. (the interdigitated capacitor has 8 fingers with 6-μm gap, 80-μm length, and 10-μm width)

	Electric field [kV/cm]	MgO		LAO	
		As-deposited	Annealed	As-deposited	Annealed
C [pF]	0	0.775 ± 0.193	0.387 ± 0.035	0.440 ± 0.028	1.281 ± 0.161
	67	0.418 ± 0.121	0.253 ± 0.031	0.354 ± 0.039	0.594 ± 0.098
Q $(= 1/\tan\delta)$	0	7 ± 1	15 ± 6	20 ± 1	6 ± 1
	67	17 ± 4	31 ± 15	46 ± 13	19 ± 3

Films which exhibit a large dielectric constant also exhibit a large % tuning, defined as $\{(C(0) - C(E))/C(0)\} \times 100$ where E is an applied electric field. General trends and maximum values for the dielectric properties for BST films are shown in Table 2. In addition to the correlation between the film dielectric constant and % tuning, it is also observed that as the dielectric constant increases, the dielectric Q decreases. The origin of the difference in the film properties on MgO and LAO are likely due to differences in film stress generated by the mismatch between the lattice parameter and thermal expansion coefficients (Table 3). The stress results in a an increase or decrease in the dimensions of the unit cell and are reflected in a change in the dielectric constant and polarization induced changes in the dielectric constant.

Figure 1 shows a possible stress field in each system caused by the lattice mismatch and the thermal expansion mismatch and annealing for epitaxial BST films on LAO and MgO. For BST films on MgO, the lattice of the film may be expanded near the interface to match to the larger lattice of the substrate and compressed on cooling by the thermal expansion mismatch ($\alpha_{BST} < \alpha_{MgO}$). When the film is post-deposition annealed, the lattice constant of the film contracts due to relaxation. Therefore, there are two competing force factors affecting the stress field of the film, which generate film strain. This force competition and the lattice contraction affect the dielectric properties of the film.

The as-deposited BST films contain significant oxygen vacancies. Annealing in flowing O_2 can fill these oxygen vacancies. This process causes a lattice contraction in the BST films. It is worthwhile to note that the study of film stress due to the film-substrate mismatch and difference in thermal expansion coefficients is complicated because of the additional change in the film lattice parameter due to changing oxygen stiochiometry. The change in the number of vacancies may increase, decrease, or screen effects that would normally contribute strongly to the overall film stress. In the interdigitated capacitor geometry, the compression, which is parallel to the applied electric field (Fig. 1) and subsequently to the polarization field for the epitaxial BST ($x = 0.5$) film, is expected to decrease the net polarization (i.e., a reduced ionic displacement). As shown in Table 1 as-deposited BST films on MgO exhibit a higher capacitance and a lower Q than both the as-deposited BST film on LAO and the annealed BST film on MgO. It may be inferred from this observation that the as-deposited BST film on MgO is under tension, which promotes the polarization of electric dipoles, and the

Table 2. Dielectric constant, measured at 1–20 GHz, tuning and Q for BST ($x = 0.5$) films on MgO and on LAO. Average film properties as well as maximum values achieved are shown

	Average		Maximum	
	MgO	LAO	MgO	LAO
ε	1000	1500	2973	3328
% Tuning (67 kV/cm)	30	50	62	75
Q	45	25	100–250	50–70

Table 3. Lattice parameters (a) and thermal expansion coefficients (α) of MgO and LAO substrates and bulk BST ($x = 0.5$)

	MgO	LAO	Bulk BST ($x = 0.5$)
a [Å]	4.213	3.787 (Pseudocubic)	3.947
α [10^{-6}/°C]	13.8	10.0	10.5

annealed film is under compression, which constrains the polarization [13–15].

This opposite behavior is observed for BST films deposited onto LAO is because the lattice parameter and the thermal expansion coefficient for LAO are smaller than for BST. This interpretation of the strain induced modification of the dielectric properties of the BST film is consistent with several reports on the study of stress on the dielectric constants for bulk ferroelectric and incipient ferroelectric materials. For bulk $BaTiO_3$ [15] $SrTiO_3$ [14] and $KTaO_3$ [13,16] pressure induced changes were observed in the dielectric constant, which was shown to decrease under compression and increase in extension. At the present time we can only discuss the effect in thin films qualitatively as we do not know exactly the zero stress state for the thin films. We have identified forces that are both compressive and tensile, however, we do not have well defined equilibrium position with which to reference the transition between a film under tension to a film under compression. As the lattice parameter decreases, the ionic displacement is reduced which results in lower net polarization. This decrease in polarization lowers the dielectric constant, which results in lower dielectric loss as expected from the Kramer-Krönig relationship. The change in dielectric properties with the lattice parameter is in agreement with literature reports on the cell volume effect in BST system [17]. In that study, the authors observed that a decrease in lattice parameter leads to decrease in T_C and dielectric loss. The decrease in T_C means lower dielectric constant, lower tuning and lower dielectric loss for our BST system (e.g., $x = 0.5$) measured at room temperature. Our results are consistent with this as we observe that the increase in the % tuning is related to the increase in the dielectric constant.

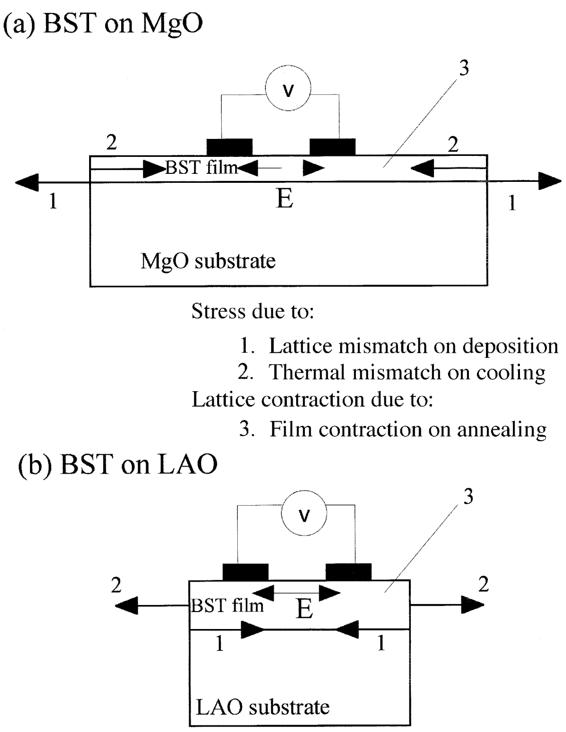

Fig. 1. Schematic diagrams of a possible force factors affecting the stress field of BST ($x = 0.5$) films (a) on MgO and (b) on LAO.

Stress in the epitaxially grown BST films can be observed directly from the X-ray diffraction. Using XRD we have measured the lattice parameters along the surface normal (c) and in the plane of the film (a) which we would expect to be the same ($a = c$) in the absence of any stress or stoichiomnetry deficiency in the film. To measure the in-plane lattice parameters in a (1 0 0) epitaxial BST film, asymmetric X-diffraction scans were made with mixed *h,k,l* indices such as (2 0 4) and (1 1 3). It is expected that for BST($x = 0.5$) at room temperature, the material should be in the paraelectric phase and therefore cubic. However, from an analysis of the XRD data, it is observed that the films unit cell is tetragonally distorted, with the in plane lattice parameter (a) enlarged relative to the surface normal. The calculated lattice parameters and tetragonal distortion for BST films deposited on MgO as are shown in Fig. 2. The distortion is largest for thin films but remains nearly constant for thicknesses above 800 Å. For thickness above 800 Å, the distortion

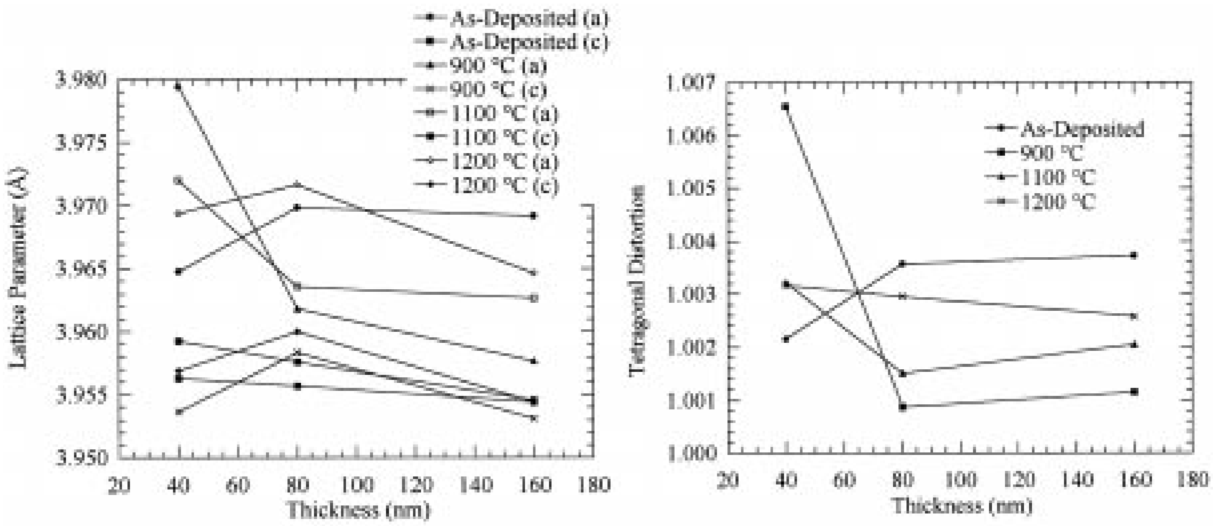

Fig. 2. (a) Lattice parameters along in-plane and surface normal directions, and (b) tetragonal distortion ratios(c/a) of BST films on MgO with different thicknesses and different annealing temperatures.

is largest in the as-deposited films. A large decrease in the distortion is observed for films annealed at 900°C which then gradually increases as the annealing temperature increases.

The changes in the film structure during a post deposition anneal are due almost entirely to variations in the in-plane lattice parameter, as shown in Fig. 3. For BST films deposited onto MgO and LAO substrates, almost no change is observed in the normal lattice parameter however, significant changes are observed in the in-plane parameter. The dielectric constant for the deposited film is also strongly correlated with the changes in the lattice parameter of the film, as shown in Fig. 3. Two important characteristics of the dielectric properties of BST films on MgO and LAO are observed. The first is that films on both substrates show a strong correlation between film structure (lattice parameter) and dielectric constant. The second is that the effect of a low temperature anneal (≤ 1000°C) is different, i.e., the dielectric constant for films deposited on MgO is decreased

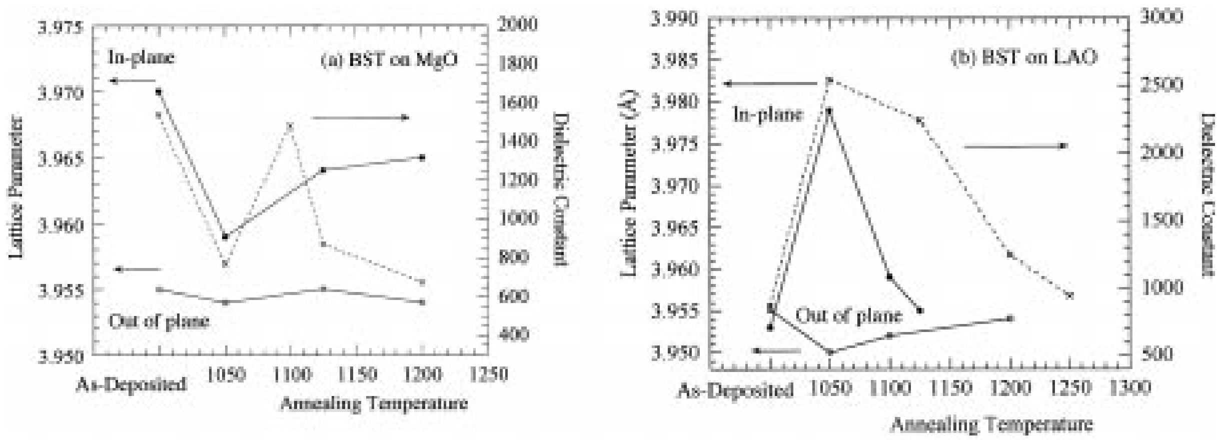

Fig. 3. Lattice parameter and dielectric constant changes with annealing temperature for $\sim 0.2\,\mu$m thick BST ($x = 0.5$) films deposited (a) on MgO and (b) on LAO.

while the opposite behavior is observed for films deposited onto LAO.

To remove the stress observed in the deposited BST films, an amorphous BST buffer layer was first deposited on to the dielectric substrate. The substrate was then heated to 750°C where the remainder of the 5000 Å thick BST films was deposited. An analysis of the X-ray diffraction pattern indicated that the film was single phase but not a single orientation. The absence of the external stress field created by the lattice mismatch between the film and the substrate should allow for a greater degree of polarization in the film (i.e., a high dielectric constant and greater tuning).

The changes in the dielectric properties of BST films deposited with and without and an amorphous buffer layer are shown in Fig. 4. For an epitaxial BST film deposited onto MgO, the % tuning is decreased while the Q is increased as the films is post annealed, as shown in Fig. 4(a). However, for a more polycrystalline film deposited onto MgO (4a and 4b), a post deposition anneal increases the % tuning and decreases the dielectric loss. The strong correlation between % tuning and dielectric loss observed in epitaxial films is now relaxed in films, which are a mixture of crystallographic orientations. That is, for films on single crystal substrates, required for epitaxial growth of all perovskite thin films, highly oriented films give rise to in degraded or extrinsic dielectric performance.

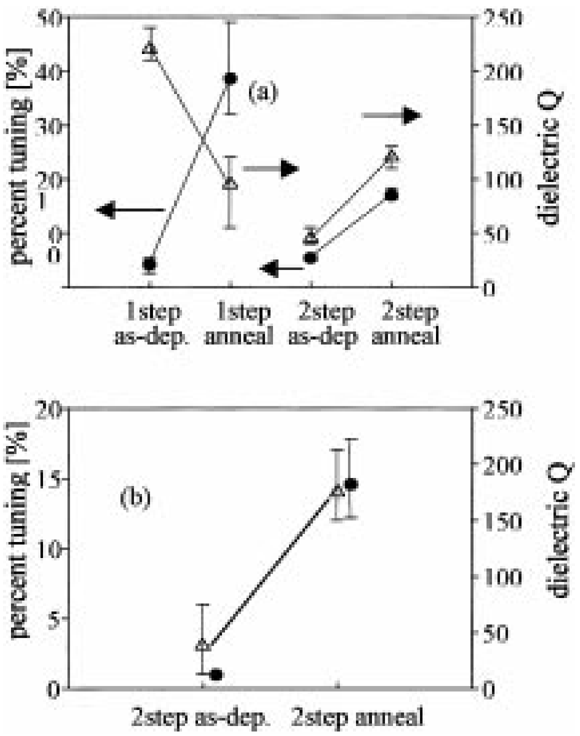

Fig. 4. Dielectric properties (1–20 GHz) for (a) 1% Mn doped BST films and (b) 1% W doped BST on MgO. 1 step and 2 step indicate film deposition without and with a BST buffer layer, respectively. ● = percent tuning, △ = dielectric Q.

4. Summary

Ferroelectric thin films are currently being used to develop a new class of tunable microwave circuits based on the electric field dependence of the dielectric constant. Single phase, (1 0 0) epitaxial $Ba_{0.5}Sr_{0.5}TiO_3$ (BST) films have been deposited onto (1 0 0) $LaAlO_3$ and MgO substrates. The dielectric properties at microwave frequencies are strongly affected by the substrate type, post deposition annealing time and temperature. For epitaxial BST films deposited onto MgO, it is observed that, after a post-deposition anneal the dielectric constant decreases and the dielectric Q increases. For epitaxial BST films deposited onto LAO, a post-deposition anneal ($\leq$ 1000°C) results in an increase in the dielectric constant and a decrease in the dielectric Q. The observed differences in dielectric properties of the epitaxial BST films on MgO and LAO are attributed to the differences in film stress which arise as a consequence of the lattice mismatch between the film and the substrate and the differences in the thermal coefficient of expansion between the film and the substrate. A thin amorphous buffer layer of BST has been used to relieve stress induced by the lattice mismatch between the film and the substrate. In stress relieved films it is possible to both increase the dielectric constant and the dielectric Q with a post deposition anneal in oxygen.

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